

## Cation exchange of swollen layered silicates

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**Abstract of GB2172883**

Flocced mineral materials, which may be utilized to prepare high temperature and water resistant articles, are prepared by treating a gellable layered swollen silicate that has an average charge per structural unit from -0.4 to -1 and which contains interstitial cations which promote swelling with a source of at least one species of multiamine derived cations.

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(54) **Cation exchange of swollen layered silicates**

(57) Flocced mineral materials, which may be utilized to prepare high temperature and water resistant articles, are prepared by treating a gellable layered swollen silicate that has an average charge per structural unit from  $-0.4$  to  $-1$  and which contains interstitial cations which promote swelling with a source of at least one species of multiamine derived cations.

**GB 2 172 883 A**

## SPECIFICATION

**Flocced mineral material and articles made therefrom**

5 This invention relates to flocced mineral materials, a process for their manufacture, and articles made therefrom, especially sheet materials. 5

Papers and/or sheets may be produced from water-swellaable inorganic materials and, in particular, swollen silicate gels. For example, United States Patent No. 4,239,519 is directed to the preparation of synthetically derived, inorganic, crystal-containing gellable, water-swellaable sheet silicates and articles, 10 such, for example, as papers, fibers, films, boards, and coatings, produced therefrom. These asbestos-free papers and/or sheets exhibit good high temperature stability and good chemical resistance. Furthermore, 10 since asbestos fibers are not utilized in their manufacture, such articles will not have the health hazards which are associated with asbestos-containing articles.

U.S. Patent Nos. 4,239,519 teaches a method for making the precursor gellable silicates used to produce 15 said papers or sheet articles, involving three fundamental steps: (a) a fully or predominantly crystalline body is formed which contains crystals consisting essentially of a lithium and/or sodium water-swellaable mica selected from the group of fluorhectorite, hydroxyl hectorite, boron fluorphlogopite, hydroxyl boron 15 phlogopite, and solid solutions between these and other structurally compatible species selected from the group of talc, fluortalc, polyolithionite, fluorpolyolithionite, phlogopite, and fluorphlogopite; (b) that body is 20 contacted with a polar liquid, normally water, to cause swelling and disintegration of the body accompanied by the formation of a gel; and (c) the solid:liquid ratio of the gel is adjusted to a desired value depending upon the application therefor. Glass-ceramics are the preferred crystalline starting bodies. Those products are then contacted with a source of large cations, i.e., with an ionic radius larger than that of the lithium 20 cation, to cause reaction to take place between the large cations and the  $\text{Li}^+$  and/or  $\text{Na}^+$  ions from the interlayer of the crystals. 25

U.S. Patents Nos. 3,325,340 and 3,454,917 teach producing aqueous dispersions of vermiculite flaked crystals which have been caused to swell by the introduction therein of interstitial ions such as (1) alkylammonium cations having between 3 and 6 carbon atoms inclusive in each carbon groups such as methylbutylammonium, n-butylammonium, propylammonium and iso-amylammonium, (2) the cationic 30 form of amino-acids, such as lysine and ornithine, and/or (3) lithium. 30

While the articles, such as papers, sheets and films, prepared by the prior art processes set forth above exhibit excellent heat resistance and are useful in a wide variety of applications, it has been discovered that such articles generally do not exhibit good sealing characteristics, thus curtailing their use as gasket materials. The prior art articles also exhibit a certain amount of water sensitivity which is generally exhibited 35 by the articles having a considerable loss of strength and general deterioration of mechanical and electrical properties when exposed to high humidity environments or submerged in water or other polar liquids. This sensitivity to water correspondingly limits the utility of these articles in certain applications, such as, for example, head gaskets, electrical insulators, environmental protective coatings, and washable and environmentally stable building materials, 40

A related application, No. 8525561, Serial No. 2166127, discloses that fire resistant articles that do not require the use of asbestos may be made from a swollen, layered flocced silicate gel material that is prepared by utilizing an exchange cation that is selected from guanidine derivatives. Such articles were surprisingly shown to exhibit more water resistance than articles prepared by prior art processes and have excellent electrical properties. 40

It has now been unexpectedly discovered that high temperature, fire-resistant, water-resistant articles, for 45 example, sheet, paper, board, film, fiber and coating articles, which similarly do not require the use of asbestos, may be made from a swollen layered flocced silicate gel material prepared by utilizing an exchange cation that is selected from multiamine derivatives. Such articles have surprisingly been found to exhibit, in general, much improved results in tensile strength and puncture resistance tests that are 50 conducted when the articles are wet than do materials that are prepared utilizing prior art exchange cations. Furthermore, the articles made according to the present invention generally display superior electrical and mechanical properties over materials made by prior art methods. 50

With reference to heat resistance, the articles that are produced according to the present invention are completely stable to temperatures of approximately 350–400°C and maintain their structural stability to 55 approximately 800°C. 55

The term "water resistant" as used herein is not meant to imply that the articles of the present invention are waterproof or are completely impervious to water. Rather, the term is used to indicate that the materials do not substantially degrade, at least in their tensile strength and puncture resistance properties, when exposed to water.

60 In addition to being water resistant and having excellent fire and heat resistance, the articles of the present invention possess excellent electrical properties and are suitable for a variety of applications, including electrical insulators, cable wrap and, in particular, printed circuit boards. 60

The present invention accordingly provides a method of preparing a flocced mineral material that may be utilized to form a non-asbestos high temperature article that exhibits water resistance, which method 65 comprises contacting a swollen layered silicate gel that has an average charge per structural unit within the 65

range of from  $-0.4$  to  $-1$  and which contains exchangeable interstitial ions with at least one species of multiamine derived cations to effect an ion exchange reaction between at least some of the exchangeable interstitial ions and at least some of the multiamine derived cations.

Advantageously, the gelled layered silicate is a synthetic gellable silicate and the interstitial ions are  $\text{Li}^+$  and/or  $\text{Na}^+$ , and preferably the synthetic silicate is prepared by contacting a body consisting essentially of crystals of a water-swelling mica selected from fluorhectorite, hydroxyl hectorite, boron fluorphlogopite, hydroxyl boron phlogopite, and solid solutions among these and between these and other structurally compatible species selected from talc, fluortalc, polyolithionite, fluorpolyolithionite, phlogopite and fluorphlogopite, with a polar liquid, preferably water, for a time sufficient to cause swelling of the crystals accompanied with the formation of a gel.

Alternatively, the silicate is vermiculite and the interstitial ions are alkylammonium cations, the cationic form of amino-acids and/or  $\text{Li}^+$ .

The present invention also provides a flocced mineral material which comprises a swollen layered silicate gel that has an average charge per structural unit within the range of from  $-0.4$  to  $-1$ , the silicate containing at least some interstitial cations that are multiamine derivatives. The material is advantageously formed by preparing a synthetic silicate gel by the method described above and contacting the thus formed gel with at least one species of a cationic multiamine derivative to effect an ion exchange reaction between at least some of the lithium and/or sodium cations and at least some of the amine derived cations.

The cations are advantageously diamine derived cations, and are preferably 1,6-hexanediamine, N,N,N',N'-tetramethylethylenediamine, o-phenylenediamine, 1,2-diaminopropane, diaminooctane, or 2,5-tolylenediamine.

Especially when the cations are derived from a diamine, the material of the invention provides a high temperature, water resistant article with good electrical properties.

The article may be in the form of a fiber or a film.

The articles and the flocced mineral suspensions of the present invention are, in one embodiment of the invention, prepared by utilizing, as a starting material, a water-swelling sheet silicate that has an average charge per structural unit of from  $-0.4$  to  $-1$  and which contains interstitial exchangeable cations that promote swelling. The specific exchange cations in the starting material will depend on the silicate being utilized. For example, if a synthetically derived gellable silicate, which may be made according to the procedures of U.S. Patent Nos. 4,239,519, is utilized as a starting material, the exchange cations will generally be  $\text{Li}^+$  and/or  $\text{Na}^+$  ions. If a natural vermiculite dispersion, which may be made according to U.S. Patent No. 3,325,340, is utilized, the exchange cations will generally include alkylammonium cations and the other cations specified in U.S. Patent No. 3,325,340. The silicate, whether synthetic or natural in origin, will most often have morphologies that are represented by thin flakes which are generally disk, strip, and/or ribbons. Although the present invention is not limited to the use of flakes of any specific dimensions, the flakes typically have measurements which are from 500 Å to 100,000 Å, and preferably 5,000 Å to 100,000 Å in length, 500 Å to 100,000 Å in width, and less than 100 Å thick ( $1 \text{ Å} = 10^{-10} \text{ m}$ ).

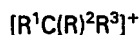
The term "charge per structural unit" as used herein refers to an average charge density as specified by G. Lagaly and A. Weiss, "Determination of Layer Charge in Mica - Type Layer Silicates", Proceedings of International Clay Conference, 61-80 (1969) and G. Lagaly, "Characterization of Clays by Organic Compounds", Clay Minerals, 16, 1-21 (1981).

The starting silicate may be made according to the afore-mentioned procedures of U.S. Patents Nos. 4,239,519, 3,325,340, or 3,434,917, or other methods which result in dissociated layer materials with charge densities in the desired ranges.

The silicate is then contacted with a source of at least one species of multiamine derived cations to effect an ion exchange reaction between the cations and the interstitial ions. This ion exchange reaction may be carried out between the cations and the silicate material to form a floc which is then utilized to form an article according to the present invention. In another embodiment of this invention, the starting silicate may be directly formed into a product, for example a lithium fluorhectorite fiber or film, by using the procedures of U.S. Patent No. 4,239,519, and a cationic exchange reaction utilizing the multiamine derived cations may be carried out with the product, such as by immersing the product in a solution of multiamine derived cations. Thus, the ion exchange reaction may be carried out *in situ* during the actual forming process for the product.

The invention accordingly further provides a method of preparing a high temperature silicate article that exhibits water resistance and good electrical properties, which method comprises contacting an article formed from gellable layered water-swelling silicate that has a charge per structural unit in the range of from  $-0.4$  to  $-1$  and which contains exchangeable interstitial ions with a source of at least one species of multiamine derived cations to effect an ion exchange reaction between at least some of the multiamine derived cations and at least some of the interstitial ions.

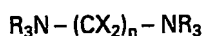
The term "multiamine derived cations", when used in reference to the exchange cations that may be utilized in the present invention refers primarily to low molecular weight, non-polymeric, di, tri and/or tetra amino functional compounds, wherein the amine moieties have been modified, such as by being protonated, to be positively charged. Diamines are the multiamine compounds of choice. Cations free from acidic groups are preferred, especially when the silicate is vermiculite, as are those that have no carbon atom bearing two or more nitrogen atoms, in particular cations free from the aminomethyleneimino group. More especially, the cations should not have the formula



wherein  $R^1$ ,  $R^2$ , and  $R^3$  are independently selected from  $NH_2$  and  $CH_3$ , provided that at least two of  $R^1$ ,  $R^2$  and  $R^3$  are  $NH_2$ , and wherein one or more of the hydrogen atoms on any one or more of  $R^1$ ,  $R^2$  and  $R^3$  may be replaced by substituents, for example  $C_1$  to  $C_5$  alkyl,  $C_2$  to  $C_5$  alkenyl or  $C_2$  to  $C_5$  alkynyl, and wherein one or more groupings of two of such substituents may be linked to form one or more rings, which may be saturated, unsaturated or aromatic.

In particular, the compound from which the cation is derived should not be guanidine, amino- or diaminoguanidine, methyl- or tetramethylguanidine, melamine, or 2-amino- or 2,6-diaminopyridine.

The preferred diamines generally correspond to the Formula



wherein each R is independently selected from hydrogen, a  $C_1$  to  $C_8$  straight or  $C_2$  to  $C_8$  branched chain alkyl group, a  $C_3$  to  $C_6$  cyclic alkyl group, or an aryl group, with the proviso that there be no more than one aryl group on each nitrogen, each X is independently selected from hydrogen, an alkyl group or an aryl group and n represents an integer from 2 to 15, with the option that, when n is 3 or more, the  $CX_2$  groups may form optionally aromatic cyclic moieties, in which case the number of X groups will be correspondingly reduced.

The flocced mineral suspensions of the present invention may be prepared, for example, by reacting, generally with agitation, a suitable silicate gel and a source of exchange cations derived from a suitable multiamine compound or compounds in order to effect an ion exchange between the multiamine derived cations and the interstitial cations in the silicate gel to form exchanged macro flocculated particles.

As stated above, one or more exchange cations may be utilized in the cationic exchange reaction. Since the various cations will give flocs, and eventually articles, with differing physical properties, the specific cation or combination of cations will be chosen by the practitioner of this invention based on the desired end use.

The terms "multiamine derived cations" or "cationic derivative" or the like are used herein to indicate that the center for cationic activity is centered on the nitrogen groups in the multiamines. Generally, this is accomplished by protonating the multiamines to form ammonium groups which are positively charged. This protonation has to take place before cationic exchange with the swollen silicate may be effected.

The flocced mineral suspension may be used to form the desired articles. The specific treatment steps applied to the floc will depend on the particular article being formed and the processes described below are examples only of procedures that may be adopted to produce a given article. For example, if the articles of the present invention are to be formed into sheet materials, the resultant exchanged floc is agitated with sufficient shear to produce a particle size distribution which leads to suitable particle packing in the sheet forming operation. Following this process the floc is optionally washed to remove any excess salt solution and the consistency of the flocced slurry is adjusted to from 0.75% to 2% solids. To promote better drainage rates on a fourdrinier wire, polyelectrolyte flocculating agents may then be added to the slurry at a level of from 0.1% to 1%, and preferably 0.2% to 0.3%, of floc solids. One example of a suitable polyelectrolyte flocculating agent is Polymyn P, which is a trademark of BASF Corporation for a polyethyleneimine.

The slurry is then fed to a papermaking apparatus wherein it is dewatered by free and/or vacuum drainage followed by pressing and drying on drum driers. The thus formed sheet material may be used in applications such, for example, as gaskets.

If desired, and depending on the intended end use of the articles, additional inert materials may be added to the flocced mineral suspension. For example, if desired one or more fibrous materials from the group of natural or synthetic, organic or inorganic, fibers may be added to the floc to improve its drainage rate and to provide an end product that has improved strength and/or handleability. For example, when the desired end products are gaskets, the fibers of choice are cellulose fibers, glass fibers, and/or Kevlar fibers (Kevlar is a trademark of Du Pont for an aromatic polyamide fiber). In addition, synthetic latex or other binders may be added to the floc to provide a product with improved strength characteristics.

Alternatively, the cationic exchange reaction may be conducted directly on a product formed from the silicate starting material. In this case, the desired additional inert materials are added to the slurry containing the silicate starting material prior to the formation of the product and, of course, the subsequent cationic exchange reaction.

It has been discovered that epoxy resins are particularly useful additives to articles formed according to the present invention. The use of such resins adds strength to the final product and, when used in conjunction with diamine exchanged floc, seems to promote a dual functionality in the multiamines, especially diamines, which act not only as exchange cations for the sheet silicate material but also as a crosslinking agent for the epoxy resins. From 1 to 80 parts by weight of epoxy resin may advantageously be utilized in producing articles according to the present invention, based on the solids weight (100 parts) of the sheet silicate starting material. The resulting product has enhanced strength, chemical resistance and dielectric properties.

In the following Examples, unless otherwise stated, the starting material utilized was a lithium fluorhectorite made according to procedures specified in U.S. Patent No. 4,239,519.

**Example 1**

This example illustrates a method of producing both a diamine exchanged fluorhectorite flocced silicate and a formed sheet prepared therefrom.

A slurry of 1,6-hexanediammonium fluorhectorite (made from the corresponding diamine) was prepared by adding 200 grams of a 10% dispersion of lithium fluorhectorite to 2 liters of 1N, 1,6-hexanediamine HCl solution. The slurry was then agitated with a high shear mixer to reduce the particle size of the resultant floc, washed and analyzed for water content and diluted to result in a 2% solids slurry. The slurry was transferred to a 11.5" × 11.5" (292 × 292 mm) hand sheet mold (manufactured by Williams Apparatus Co.) and dewatered. The resulting formed sheet was then wet pressed and dried on a drum drier. The sheet has good flexibility and performed well in the gasket sealing test.

**Example 2**

Using the procedures of Example 1, a handsheet was prepared from the following slurry:

		Wt. Percent	
15	Hexamethylene diammonium fluorhectorite	58.7	15
	NBR latex	3.2	
	Alum	2.9	
	Micro Talc	5.9	
20	Redwood Fiber	2.9	20
	Kevlar Fiber	2.9	
	Mineral Wool	23.5	

The resulting handsheet was subjected to gasket sealing tests which were electro-mechanical air leakage tests conducted according to the specifics set forth in pages 1-3 of the Society of Automotive Engineers, Inc. technical paper SAE 83022 (ISSN 0148-7191 (83/0228-0220 1983).

The results of the tests were:

	Initial Flange Pressure		Leakage rate		
	psi	mPa	(psilmin)	kPalmin	
30	570	3.93	1.389	9.577	30
	915	6.31	1.587	10.94	
	2500	17.2	0.529	3.65	

**Example 3**

This example illustrates a method of producing films of the present invention wherein the cationic exchange is made *in situ*.

A 10% solids lithium fluorhectorite gelled dispersion was prepared according to the procedures described in U.S. Patent No. 4,239,519. A film was made of this material by using a 4.5 mil (0.11 mm) Byrd applicator, which was 5 inches (127 mm) wide, to draw down a 4.5 mil thick wet film of the dispersion on a glass plate. The glass plate, with the film attached, was then immersed in a 0.25M solution of 1,6-hexane-diamine HCl solution to cause a cation exchange between the 1,6-hexanediammonium cations and the fluorhectorite's interlayer cations. A skin was formed, seemingly instantaneously, on the film which indicated such an exchange was taking place. In 10 minutes the film was removed from the plate, washed in deionized water to remove residual salts, and dried. The film had good flexibility and strength retention when wet.

**Examples 4-15**

For each of these examples, the procedure of Example 3 was substantially repeated with the exchange cation (prepared from the corresponding diamine) as specified to form the corresponding film.

	Example	Exchange Cation	
50	4	N,N,N',N'-tetramethylethylenediammonium	
	5	o-phenylenediammonium	
	6	1,2-diammonium propane	
55	7	1,8-diammonium octane	55
	8	2,5-tolylenediammonium	
	9	1,7-diammonium heptane	
	10	1,9-diammonium nonane	
	11	1,5-diammonium pentane	
60	12	1,2-ethylenediammonium	60
	13	1,3-diammonium propane	
	14	1,4-diammonium butane	
	15	1,12-diammonium dodecane	

### Comparative Examples 1-3

These comparative examples illustrate fluorhectorite films that are made with various prior art exchange cations. Potassium fluorhectorite (KFH) and ammonium fluorhectorite (NH<sub>4</sub>FH) were separately prepared by the process specified in U.S. Patent No. 4,239,519. A 4.5 mil (0.11 mm) thick film was then cast from both the KFH and a NH<sub>4</sub>FH slurries. A Kymene (a trademark of Hercules, Inc. for a cationic, polyamide-epichlorohydrin resin) fluorohectorite film was also prepared by the procedure of Example 3, except that (1) a 3.0% Kymene solution was used and (2) the lithium fluorhectorite film had to be immersed in the Kymene solution for 2 hours until the resulting exchanged film was sufficiently self-supporting to be removed from the glass plate. The protonated "Kymene" fluorhectorite film is designated Comparative Example 1, the NH<sub>4</sub>FH film and the KFH film are designated Comparative Examples 2 and 3 respectively. These films, along with the films made in Examples 3 to 15, were then subjected to tensile strength and puncture resistance tests which were conducted as follows:

### Tensile Strength Measurements

Dry tensile strength measurements were determined using an Instron (trademark) Tester at 1.5 inches (38 mm) jaw separation and 0.2"/min (0.5 mm/min) crosshead speed. Wet strength measurements were made by bringing water-saturated sponges in contact with both sides of the film sample for 10 seconds while the sample was positioned in the Instron clamps just before the strength test was conducted.

### Puncture Resistance Measurements

A sample of film was secured in a retaining device which held the film securely. A stylus which could be loaded was caused to impinge on the film in the direction normal to the surface of the film and loaded with increasing weight until the stylus penetrated the film. In the wet test the film in the retaining device was submerged in deionized water for 10 seconds immediately preceding the puncture resistance test.

The results of these tests are shown in the table below; for the details of exchange cations see above.

TABLE

Film of Example No.	Tensile Strength				Puncture Resistance	
	(psi)		(mPa)		(g/mm)	
	Dry	Wet	Dry	Wet	Dry	Wet
3	16000	17000	110	117	13000	6000
4	18000	16000	124	110	11000	5100
5	13000	15000	90	103	7600	3000
6	13000	11000	90	76	14000	4200
7	12000	11000	83	76	6500	1700
8	9800	11000	68	76	6500	1800
9	7300	8800	50	61	16000	7500
10	7000	5000	48	34	3600	1400
11	6600	4400	45	30	5700	5200
12	5200	3600	36	25	1200	600
13	3300	1400	23	9.7	3500	680
14	3000	1400	21	9.7	6600	900
15	1800	2900	12	20	3100	570
Comparative Example No.						
1	7000	2700	48	19	900	260
2	3300	1400	23	9.7	3500	680
3	1100	200	7.6	1.4	3300	440

The results indicate that the films made according to the procedures of the present invention have markedly superior wet tensile strength and/or superior wet puncture resistance compared to prior art compositions.

### Fire and Smoke Resistance

A film prepared according to Example 3 was, after being dried, subjected to fire and smoke resistance tests in accordance with the procedures specified in ASTM-E-662-79. Three separate tests were made and the results are set forth below.

*Test 1 – Flammability*

(The numerical values correspond to the maximum specified optical density as per N.B.S. Technical Note No. 708.)

5	Flaming Mode	0	5
	Smoldering Mode	0	

*Test 2*

10	Oxygen Index Type C ASTM D2863-77		10
	Critical Oxygen Index – 100% O <sub>2</sub>		

*Test 3*

Radiant Panel ASTM-E162-79

15	Flame Spread Factor	1.00	15
	Heat Evolution	0.0	
	Flame Spread Index	0.0	

*Electrical Properties*

20	A film of Example 3 was, when dried, tested for the dielectric constant and dissipation factor using the procedures of ASTM D150 and for dielectric strength using the procedures of ASTM D149. The results, set forth below, indicate the film has utility in a variety of electrical insulating properties.		20
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		<i>Dielectric Constant</i>	<i>Dissipation Factor</i>	
25	100 Hz at 25°C	26.53	0.288	25
	100 Hz at 300°C	37.9	0.37	
	100 Hz return to 25°	10.7	0.049	
	100 kHz at 25°C	12.19	0.153	
30	100 kHz at 300°C	15.0	0.202	30
	100 kHz return to 25°C	9.52	0.024	

Dielectric strength measured at 577v/mil (22.7 Kv/mm).

35	<i>Comparative Examples 4 and 5</i>	35
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These examples illustrate using, as a starting material, silicate materials which fall outside the scope of the present invention in their charge per structural unit and their physical measurements.

40	For Comparative Example 4, a 10% aqueous dispersion was made from a natural hectorite obtained from the source clay minerals depository of the Clay Minerals Society, Bloomington, Indiana. For Comparative Example 5, a 10% aqueous dispersion was made utilizing sodium montmorillonite, which was obtained from the same source. In each example, a film was drawn down using the procedures set forth in Example 3. The glass plates were then immersed for 10 minutes in a 0.25 M 1,6-diammonium hexane solution. In both instances, a coherent film was not produced.	40
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45	<i>Example 16</i>	45
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This example illustrates a method of preparing a film of the present invention utilizing a vermiculite starting material:

50	A 10% solids suspension of n-butylammonium vermiculite, which was prepared according to the procedures specified in U.S. Patent No. 3,325, 340, was cast as a film on a glass plate according to the procedure set forth in Example 3. The glass plate, with the film attached, was immersed for 10 minutes in a 0.25 M 1,6-hexanediamine HCl solution. The resulting film was removed from the plate, washed, and dried. The film displayed wet strength in the tensile strength and puncture resistance tests that a comparable unexchanged vermiculite film does not display.	50
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55	<i>Example 17</i>	55
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60	This example illustrates preparing fibers utilizing the method of the invention. A 15% solids suspension of lithium fluorhectorite (prepared as above) was extruded through an 11 mil (0.28 mm) opening needle into a 2N solution of 1,6-hexanediamine HCl. The extruded fiber was carried by a porous belt and delivered to a second bath of 2N 1,6-hexanediamine HCl. The fiber so produced was washed by submersion in deionized water and dried. The resultant fiber was strong and flexible.	60
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*Example 18*

65	This example illustrates the addition of an epoxy to sheet silicate composites. Codispersions of the diglycidyl ether of bisphenol A (DGBA) and lithium fluorhectorite (LiFH) were prepared by adding the epoxy to a 10% (solids) aqueous lithium fluorhectorite dispersion. The codispersion	65
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was then mixed using a high shear process. The codispersions were formed in the following ratios of LiFH to DGBA:

1. 100 g. 10% solids LiFH dispersion (10 g. LiFH solids): 0.1 g epoxy (approx. 1% on solids basis).
2. 100 g. 10% solids LiFH dispersion: 1.1 g. epoxy (approx. 11%).
- 5 3. 100 g. 10% solids LiFH dispersion: 2.5g. epoxy (approx. 25%). 5

The films were prepared by producing 4.5 mil (11 mm) wet films on glass plates with a Byrd applicator and immersing the film in a 0.25M hexamethylenediamine HCl soln. at a pH of 7.0. The resulting films had the good wet strength characteristic of hexamethylene diammonium exchanged fluorhectorite. The film was washed with deionized water to remove excess hexamethylene diamine HCl and dried at 60°C. The dry films, which were flexible, were heated to 150°C for 3 hours. The resulting films exhibited increased rigidity as would be expected with epoxy curing. Therefore, it appears that the hexamethylenediammonium cation is effected in performing both the layered silicate exchange function and epoxy curing.

In an alternative method of making the articles, epoxy/fluorhectorite codispersions as described above were converted to floc form through the addition of the codispersion to a 0.25M hexamethylenediamine HCl solution with agitation. After washing the excess hexamethylenediamine HCl from the floc it was adjusted to a solids content of 2% and subjected to high shear mixing to reduce the particle size. The resulting material was transferred to a nonporous mold and allowed to dry to coherent flexible films of approximately 10 mils (0.25 mm) thickness.

The films were hot pressed at 150°C for 3 hours and became more rigid.

## 20 CLAIMS 20

1. A method of preparing a flocced mineral material, which comprises contacting a swollen layered silicate gel that has an average charge per structural unit within the range of from  $-0.4$  to  $-1$  and which contains exchangeable interstitial ions with at least one species of multiamine derived cations to effect an ion exchange reaction between at least some of the exchangeable interstitial ions and at least some of the multiamine derived cations.

2. A method of preparing a silicate article which comprises contacting an article formed from a gellable layered water-swelling silicate that has a charge per structural unit within the range of from  $-0.4$  to  $-1$  and which contains exchangeable interstitial ions with a source of at least one species of multiamine derived cations to effect an ion exchange reaction between at least some of the multiamine derived cations and at least some of the interstitial ions.

3. The method of claim 1 or claim 2, wherein the multiamine derived cations are diamine derived cations.

4. The method of claim 3, wherein the diamine is hexanediamine, N,N,N',N'-tetramethylethylenediamine, o-phenylenediamine, 1,2-diaminopropane, diaminooctane, or 2,5-tolylenediamine.

5. The method of any one of claims 1 to 4, wherein the layered silicate is a synthetic silicate and the interstitial ions are  $\text{Li}^+$  and/or  $\text{Na}^+$ .

6. The method of claim 5, wherein the synthetic silicate is prepared by contacting a body consisting essentially of crystals of a water-swelling mica selected from fluorhectorite, hydroxyl hectorite, boron fluorphlogopite, hydroxyl boron phlogopite, and solid solutions among these and between these and other structurally compatible species selected from talc, fluortalc, polyolithionite, fluorpolyolithionite, phlogopite and fluorphlogopite, with a polar liquid for a time sufficient to cause swelling of the crystals accompanied with the formation of a gel.

7. The method of claim 6, wherein the crystals are fluorhectorite.

8. The method of claim 7, wherein the polar liquid is water.

9. The method of any one of claims 1 to 4, wherein the silicate is vermiculite and the interstitial ions are alkylammonium cations, the cationic form of amino-acids and/or Li ions.

10. A flocced mineral material which comprises a swollen layered silicate gel that has an average charge per structural unit in the range of from  $-0.4$  to  $-1$ , said silicate containing at least some interstitial cations that are multiamine derivatives.

11. The material of claim 10, wherein the multiamine derived cations are as specified in claim 3 or claim 4.

12. The material as claimed in claim 10 or claim 11, wherein the silicate gel is prepared by the procedure specified in claim 6, followed by contacting the thus formed gel with at least one species of a cationic multiamine derivative to effect an ion exchange reaction between at least some of the lithium and/or sodium cations and at least some of the amine derived cations.

13. The material of claim 10 or claim 11, wherein the silicate is vermiculite.

14. An article comprising a swollen layered silicate that has an average charge per structural unit within the range of from  $-0.4$  to  $-1$ , said silicate containing at least some interstitial cations that are multiamine derivatives.

15. An article as claimed in claim 12, wherein the multiamine is a diamine.

16. The article of claim 14 or claim 15, further comprising an epoxy resin.

17. The article of any one of claims 14 to 16, which is in the form of a sheet material.

18. The article of any one of claims 14 to 16 which is in the form of a fiber.

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19. The article of any one of claims 14 to 16, which is in the form of a film.
20. An electrical component comprising an article as claimed in any one of claims 14 to 19.
21. A method as claimed in claim 1 or claim 2, carried out substantially as described in any one of Examples Nos. 1 to 18 herein.
- 5 22. A material as claimed in claim 10 or an article as claimed in claim 14, substantially as described in any 5 one of Examples 1 to 18 herein.
23. Any novel feature hereinbefore described or any novel combination of hereinbefore described features.

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